GeoStudies

GeoStudies 1: 27–42 (2024)
DOI: 10.3897/geostudies.1.e115530

Research Article

Thermomagnetic analysis applied for identification of lithogenic and pedogenic iron oxides in topsoils from Bulgaria

Neli Jordanova[1], Diana Jordanova[1]

1 *National Institute of Geophysics, Geodesy and Geography, Bulgarian Academy of Sciences, Acad. G. Bonchev str., block 3, 1113 Sofia, Bulgaria*
Corresponding author: Neli Jordanova (neli_jordanova@hotmail.com)

Abstract

Identification of magnetic minerals, which determine the magnetic properties of natural rocks, sediments and soils, is of crucial importance for any further interpretation of their magnetic signature in environmental or paleogeographical context. One of the major and widely used methods for determination of kind of magnetic phases in natural materials is by obtaining the Curie/Neel temperature of the respective magnetic mineral. In this contribution, we report a set of thermomagnetic measurements of high-temperature behavior of magnetic susceptibility for topsoils from the territory of Bulgaria, aiming to reveal the pedogenic and lithogenic signature. The data are considered and reported in respect to the parent rock type. Our results suggest that pedogenic magnetic minerals are represented mainly by fine-grained maghemite and/or hematite with possible Al-substitutions in the crystal lattice. This phase is expressed on the heating run of the thermomagnetic curve as a "hump" with a maximum at 250–300 °C. Coarse-grained magnetite is identified as a dominant lithogenic magnetic mineral. Hematite's presence in a sub-set of red-colored soils is confirmed by additional analyses of isothermal remanence acquisition curves. Two hematite coercivity components were identified, related to pedogenic and lithogenic origin, respectively.

Key words: soil magnetism, magnetic minerals, magnetite, hematite

OPEN ACCESS

Academic editor: M. K. Avramova
Received: 9 November 2023
Accepted: 13 February 2024
Published: 21 May 2024

Citation: Jordanova N, Jordanova D (2024) Thermomagnetic analysis applied for identification of lithogenic and pedogenic iron oxides in topsoils from Bulgaria. GeoStudies 1: 27–42. https://doi.org/10.3897/geostudies.1.e115530

Copyright: © Neli Jordanova & Diana Jordanova. This is an open access article distributed under terms of the Creative Commons Attribution License (Attribution 4.0 International – CC BY 4.0).

Introduction

Iron (Fe) is a ubiquitous element in Earth's crust and especially in its surface soils cover. Fe exists in soils in various forms – it is incorporated into the structure of clay minerals, resides in the detrital rock-forming minerals, or exist in forms of secondary pedogenic (oxy)hydroxides (Cornell and Schwertmann 2003). During the modern Anthropocene era (Certini and Scalenghe 2011), Fe in soils can also have anthropogenic origin sourced from iron-containing emissions of different industrial factories, traffic and agriculture (Hoffmann et al. 1999; Magiera et al. 2011; Declercq et al. 2020). Environmental- and rock-magnetism are widely applied methods for investigation of the origin and environmental significance of iron (oxy)hydroxides in soils and sediments (Thompson and Oldfield 1986; Evans and Heller 2003), based on their magnetic properties. Soil's magnetism is due to the presence of strongly magnetic iron oxides and is a phenomenon, which is recognized long ago (Mullins 1977). The most important environmental

factors, controlling the form of iron oxyhydroxides in soils, are temperature and precipitation (Jenny 1941), being the major climate-related parameters. Aside from anthropogenic input of strongly magnetic Fe-oxides, different theories on their origin in soils are developed through time (Dearing et al. 1996), including: 1) iron oxide grains, inherited from parent rock during weathering; 2) pedogenically formed through abiotic processes; 3) pedogenically produced by Fe-mediating bacteria; 4) intra-cellularly produced by magnetotactic bacteria. Still, no unique theory is able to explain the varieties of iron forms in soils and a combination of all proposed mechanisms seem to account for the observed magnetic properties of soils from different environmental settings.

Magnetic enrichment of topsoils from the temperate climatic belt in the Northern hemisphere is a well established phenomenon (Maher 1998) and the hypotheses existing about the origin of soil's magnetic enhancement, mentioned above, were developed on the basis of their properties. Magnetic susceptibility (K) is the simplest magnetic parameter, reflecting the ability of a material to be magnetized when it is placed in an external magnetic field. In case of isotropic medium, M = K.H, where M is the induced magnetization in the material and H is the strength of the applied field. In order to entangle the most probable mechanism, responsible for soil's magnetic properties, it is of crucial importance to discriminate pedogenic magnetic minerals from those of lithogenic origin. Thermomagnetic analysis, and in particular high-temperature behavior of magnetic susceptibility, is a widely applied method for identification of the magnetic minerals through their Curie (Neel) temperatures (O'Reilly 1984). In the present contribution, we report results from thermomagnetic analysis of a collection of topsoils from Bulgaria, developed on different parent materials and in different climate conditions, in order to evaluate the relative contribution of lithogenic vs pedogenic magnetic minerals. In addition to thermomagnetic analyses, results from coercivity un-mixing analysis of curves of step-wise acquisition of isothermal remanence (Maxbauer et al. 2016), are reported, aiming at better evaluation of the contribution of hematite (α-Fe_2O_3) to the soil's magnetism.

Materials and methods

Soil collection studies included 42 sites (Fig. 1) from which soil samples were gathered from the uppermost 0–20 cm depth. Soil material was thoroughly mixed for obtaining homogeneous sample. The samples were a selected subset of national-scale collection, consisting of 511 sampling locations for soil's magnetic characterization (Jordanova 2016; Jordanova et al. 2016). Samples for the present study were chosen as representative for the major soil groups. At each site, field magnetic susceptibility $K_{topsoil}$ was measured using handheld KT-5 kappameter (SatisGeo s.r.o.). Final value of K was taken as the average of 5 to 10 single measurements done in an area of 2 m^2. Sampling procedure was described in detail in Jordanova et al. (2016). Site's geographical location, lithology, soil type and magnetic susceptibility (field-measured topsoil and rock outcrops (where available) and soil's mass-specific) was summarized in Suppl. materials 1, 2.

In the laboratory, soil material was air-dried, gently crushed and passed through 2-mm sieve. Magnetic susceptibility K was measured using KLY-2

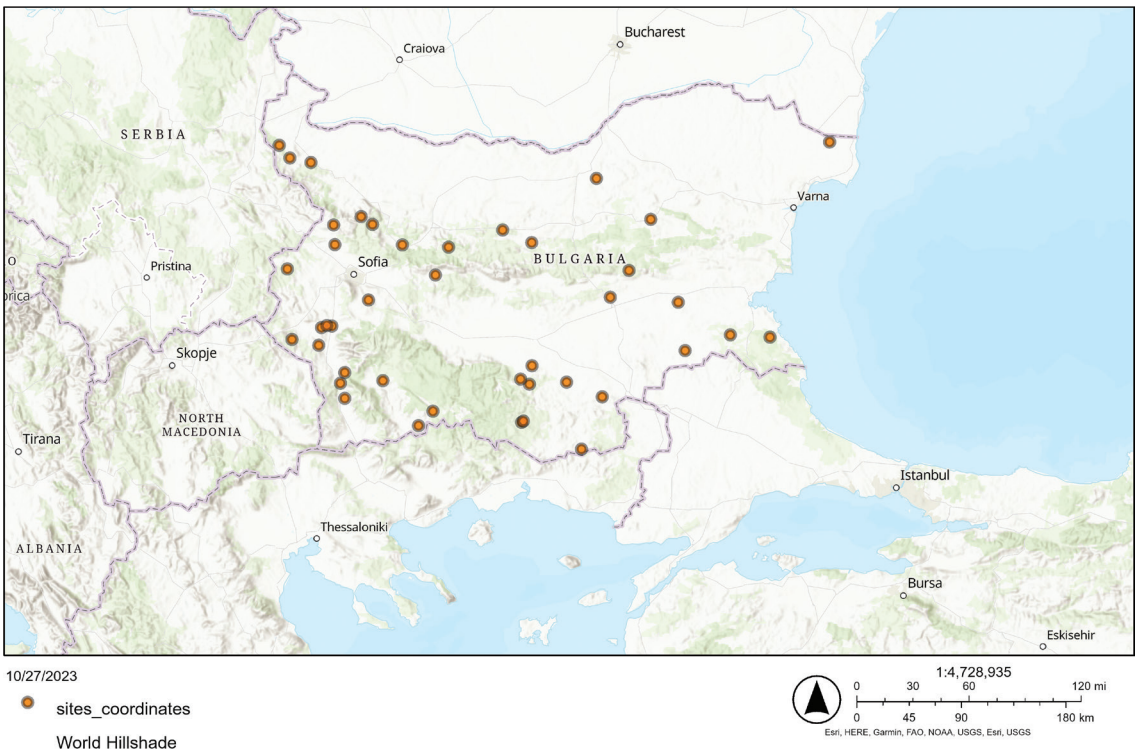

Figure 1. Sampling site's location depicted on the map.

kappabridge (AGICO Ltd., Czech Republic) and mass-specific susceptibility (χ) was obtained by dividing K to the sample's mass. Sieved soil material was used for running thermomagnetic analyses using KLY-2 kappabridge (AGICO Ltd., Czech Republic), equipped with CS-23 high-temperature non-magnetic furnace with a special platinum thermometer. Small amount of soil material (sample mass varying between 0.02–0.06 g) was placed in a quartz glass test tube of the instrument. Heating run was performed by continuous heating from room temperature up to 700 °C, employing fast heating rate (11 °C/min). Fast heating rate was chosen because it provides more sensitive information about the mineralogical transformations during heating, while using medium and slow heating rate the transformations occur more slowly and are smeared on the heating curve (Jordanova and Jordanova 2016). Magnetic susceptibility was registered automatically at each ~ 3 °C. After reaching the maximum temperature, cooling run from 700 °C to 40 °C was also recorded. Data acquired was processed using specialized software CUREVAL (AGICO Ltd., Czech Republic). Isothermal Remanent Magnetization (IRM) for selected samples (showing mainly red coloring and thus potentially containing hematite) was step-wise induced up to a maximum field of 5 Tesla. After each magnetization step IRM was measured using JR6A automatic spinner magnetometer (AGICO Ltd., Czech Republic) and IRM-acquisition curves were obtained. The data were further processed with MAX UnMix software (Maxbauer et al. 2016) to separate the main remanence coercivity components using a combination of cumulative Gaussian functions (Robertson and France 1994; Kruiver et al. 2001). Parameters "relative contribution to the total IRM" (% contr.), the field at which half of the Saturation IRM is acquired ("Bh" in log-units and in "mT"), and the width of the distribution (one standard deviation of the logarithmic distribution) expressed through the dispersion parameter "DP" (Kruiver et al. 2001) were estimated for each sample.

Results and discussion

Detailed magnetic characterization of the national-scale topsoil collection (Jordanova et al. 2016) revealed that the most important factor, controlling the magnetic properties of soil at this scale, is lithology. Such a conclusion is also drawn in other works, reporting wide-scale study area or collection of soils, developed on various rock types (Fialova et al. 2006; Hanesch et al. 2007; Thévéniaut and Clarke 2013; Sardoo et al. 2023). Considering the sub-collection used in the present study, a confirmation of this general observation is the obtained log-linear regression between the field-measured topsoil magnetic susceptibility ($K_{topsoil}$) and the mass-specific magnetic susceptibility of rock pieces gathered from rock outcrops at the respective sampling site (Fig. 2).

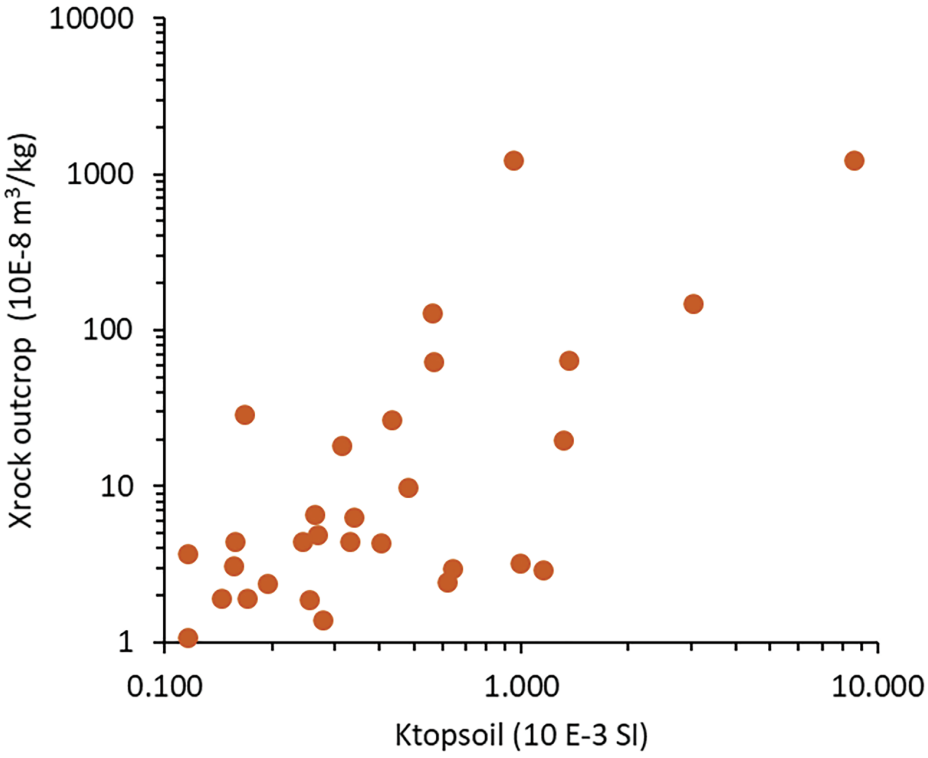

Figure 2. Mass-specific magnetic susceptibility of rocks (Xrock outcrop) vs. field-measured magnetic susceptibility of topsoils ($K_{topsoil}$) for the collection studied.

In this comparison, mass-specific value of magnetic susceptibility of rock is considered in order to avoid K-dependence on the surface roughness during field measurements. Based on the finding that lithology is a dominant influencing factor, samples were grouped into six major sub-groups, as follows: 1) soils, developed on granites (7 sites); 2) soils developed on volcano-sedimentary parent materials (including tuffs) (4 sites); 3) soils developed on limestones and marls (10 sites); 4) soils, developed on sandstones (11 sites); 5) soils, developed on alluvial/delluvial deposits and loess (5 sites); 6) soils, developed on metamorphic rocks (5 sites). This general grouping will be further used for consideration of thermomagnetic analyses of soils.

High-temperature behavior of magnetic susceptibility for topsoils, developed on granites, are shown in Fig. 3.

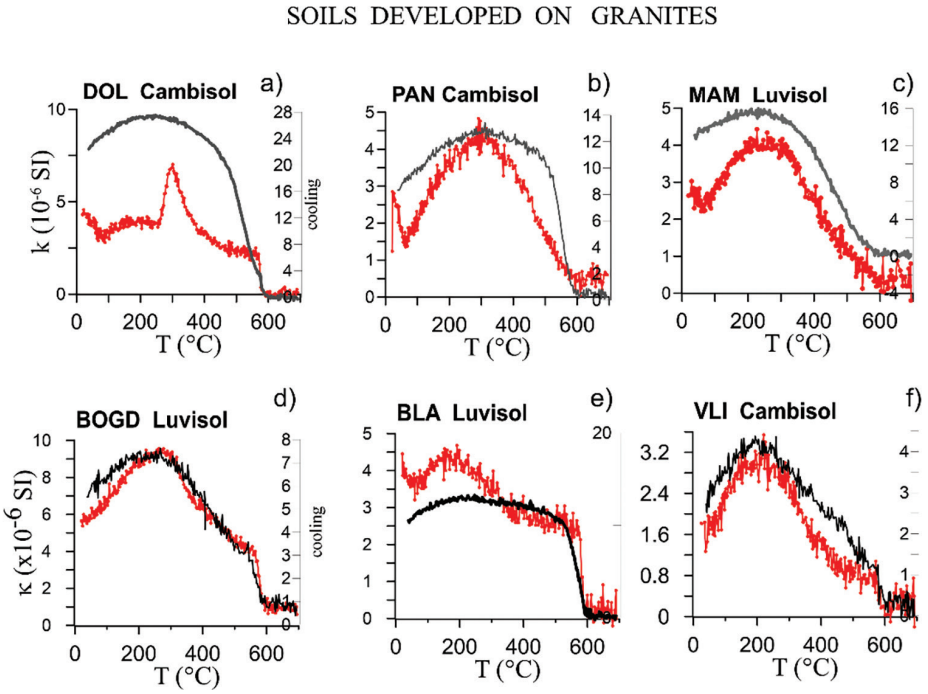

Figure 3. High temperature behavior of magnetic susceptibility for representative samples of soils, developed on granites. Soil type is indicated for each sample next to the sample's name. Heating performed in air, using fast heating rate (11 °C/min) and small sample's mass (20–60 μg). Heating run is shown in red, cooling run – in black. Right-hand Y-axis relates to k-values on the cooling curve.

As mentioned in the methods section, thermomagnetic analyses were carried out using relatively small amount of material. This fact has important implications for the shape and characteristics of the k-T heating-cooling curves, as discussed in detail in Jordanova and Jordanova (2016). In the latter study, the authors found that using a small sample mass in thermomagnetic runs results in weaker changes in K, provoked by thermal transformations in Fe-bearing minerals during heating. On the other hand, a bigger sample's mass creates local anaerobic conditions due to the presence of organic compounds in soil, which leads to strong expression of mineral transformations during heating. Based on the above considerations, we regard the K-behavior in the temperature range ~100–300 °C (wide maxima in K at 200–300 °C (Fig. 3b–f)) as reflecting the presence of Fe-oxide phase with such Tc (or unblocking temperature, Tub), rather than as expression of a thermal transformation. This phase can be related to the presence of pedogenic maghemite fraction of grains with sizes spanning the single-domain – superparamagnetic (SD-SP) magnetic grain size range, as proposed recently by Zhang and Appel (2023). Another possibility is to link this phase to fine-grained hematite with abundant ion substitutions in the crystal lattice (Jiang et al. 2014). Taking into account that the soil types in this group are mainly Luvisols and Cambisols (Fig. 3), characterized by pedogenic formation of maghemite (Jordanova 2016), it supports our hypothesis

for the presence of pedogenic maghemite fraction. Another magnetic phase, revealed on the heating k-T curves has a Tc of ~580 °C, attributable to magnetite (Fe_3O_4). This phase has bigger share in Luvisols BOGD and BLA (Fig. 3d, e) and smaller – in Cambisols DOL and VLI (Fig. 3a, f). Considering the sharp drop in K at the Tc of magnetite (Fig. 3a, d, e, f), it can be supposed that magnetite exists as coarse multidomain (MD) grains (Dunlop and Özdemir 1997). Therefore, magnetite phase can be attributed to lithogenic minerals inherited from the parent rocks (granites). The dominant presence of MD magnetite in granites from Bulgaria is reported in several works (Georgiev et al. 2009; Henry et al. 2011). Sharp drop in K at T ~100 °C (Fig. 3a, b, c, e) is related to the presence of Fe-hydroxide goethite (α-Fe_2O_3) which has a Neel temperature T_N of 120 °C (Dunlop and Özdemir 1997). Sample DOL shows strong thermal transformation at ~270 °C (Fig. 3a) with creation of magnetite, which can be linked to transformation behavior of Fe-hydroxides ferrihydrite or lepidocrocite (γ-FeOOH) in the presence of organic matter (Hanesch et al. 2006). Cooling curves for all samples, except BOGD and VLI show creation of new strongly magnetic magnetite phase upon heating to 700 °C (Fig. 3).

Thermomagnetic curves for soils, developed on volcano-sedimentary materials are presented in Fig. 4.

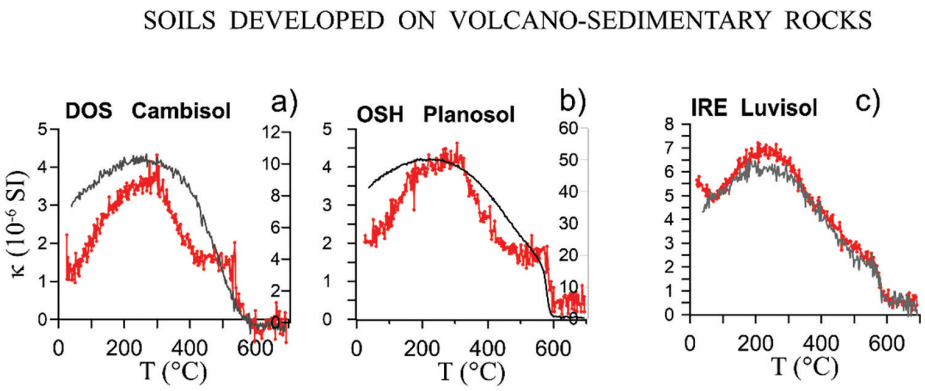

Figure 4. High temperature behavior of magnetic susceptibility for representative samples of soils, developed on volcano-sedimentary rocks. Heating run is shown in red, cooling run – in black. Right-hand Y-axis (when present) relates to k-values on the cooling curve.

Topsoils, developed on volcano-sedimentary rocks, exhibit thermomagnetic behavior (Fig. 4), similar to that of soils, developed on granites (Fig. 3). Again, two main magnetic phases are outlined – one with Tc ~ 300 °C, attributable to fine-grained pedogenic maghemite (Zhang and Appel 2023) or fine grained hematite (Jiang et al. 2014), and a second one, characteristic for coarse-grained lithogenic magnetite with Tc of 580 °C. Low Tc~100 °C is also detected in sample IRE (Fig. 4c), indicative of goethite. For this sample heating-cooling run does not cause creation of new magnetic phase and the cooling curve coincides with the heating one, except for the part, indicative of goethite. For this reason, the Tc~300 °C in this particular case can be related to the presence of titanomagnetite with high Ti content, which is a common rock-forming mineral in volcanic rocks (O'Reilly 1986). Similarity in thermomagnetic behavior of soils, developed on granites and on volcano-sedimentary rocks is consistent

with the magmatic origin of their parent lithology (high-temperature intrusive or extrusive rocks). Relatively big part of the topsoils studied are developed on limestones / marls. Representative thermomagnetic curves are shown in Fig. 5.

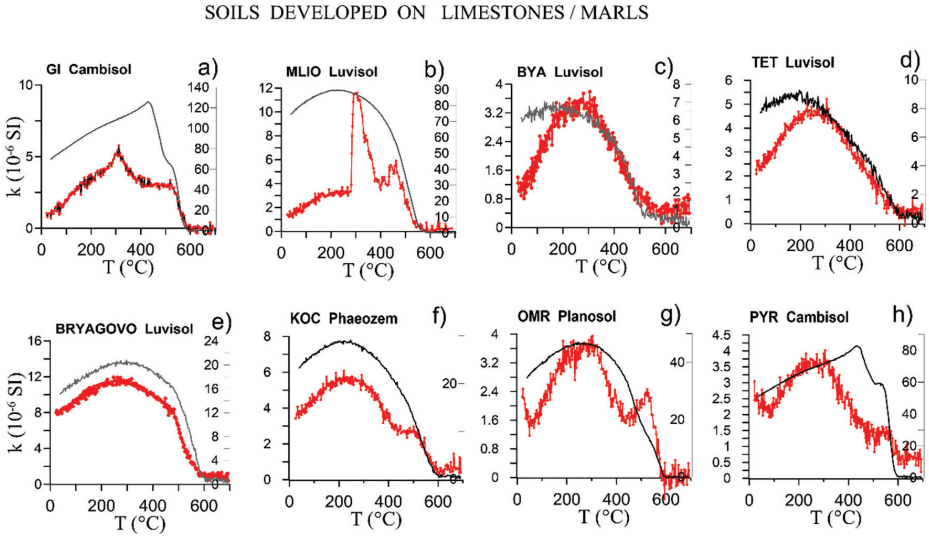

Figure 5. High temperature behavior of magnetic susceptibility for representative samples of soils, developed on limestones/ marls. Heating run is shown in red, cooling run – in black. Right-hand Y-axis relates to k-values on the cooling curve.

Thermomagnetic curves for soils developed on limestones or marls show various shapes, indicative of different magnetic minerals and/or thermal transformations (Fig. 5). Samples GI and MLIO (Fig. 5a, b) clearly indicate sharp thermal transformation at ~300 °C with production of a big amount of secondary magnetite, as revealed by one-order of magnitude stronger signal on cooling. Such strong transformation might be related to thermal destruction of the iron hydroxide ferrihydrite (Hanesch et al. 2006). Luvisol samples from sites BYA and TET (Fig. 5c, d) show similar heating-cooling curves, characterized by one well expressed wide maximum at 250–300 °C and susceptibility decrease to zero at magnetite's Tc of ~580 °C. This magnetite is preserved on the cooling curve, but without the maximum at ~300 °C. This observation suggests that most probably the thermomagnetic curves indicate the presence of fine-grained magnetite, which upon heating is subjected to grain-size change. Therefore, we attribute the phase with the maximum at ~300 °C to pedogenic magnetite. However, taking into account that both soils are of Luvisol type and exhibit reddish coloring, another hypothesis is linking it to very fine-grained hematite (Jiang et al. 2014), but it needs further investigations.

Soil samples, shown at Fig. 5f–h display similar thermomagnetic curves with two magnetic phases present – the above discussed fine-grained magnetite with unblocking temperature (Tub) ~ 300 °C and well expressed magnetite with Tc ~ 580 °C. Similarly to samples in Fig. 5a, b, again strong thermal transformation(s) occur on heating above 600 °C and new magnetite phase appears (Fig. 5f–h). Mineral transformations on cooling might partly result from the thermal transformations in Ca-bearing bedrock (limestone, marl) (Duminuco et al. 1998).

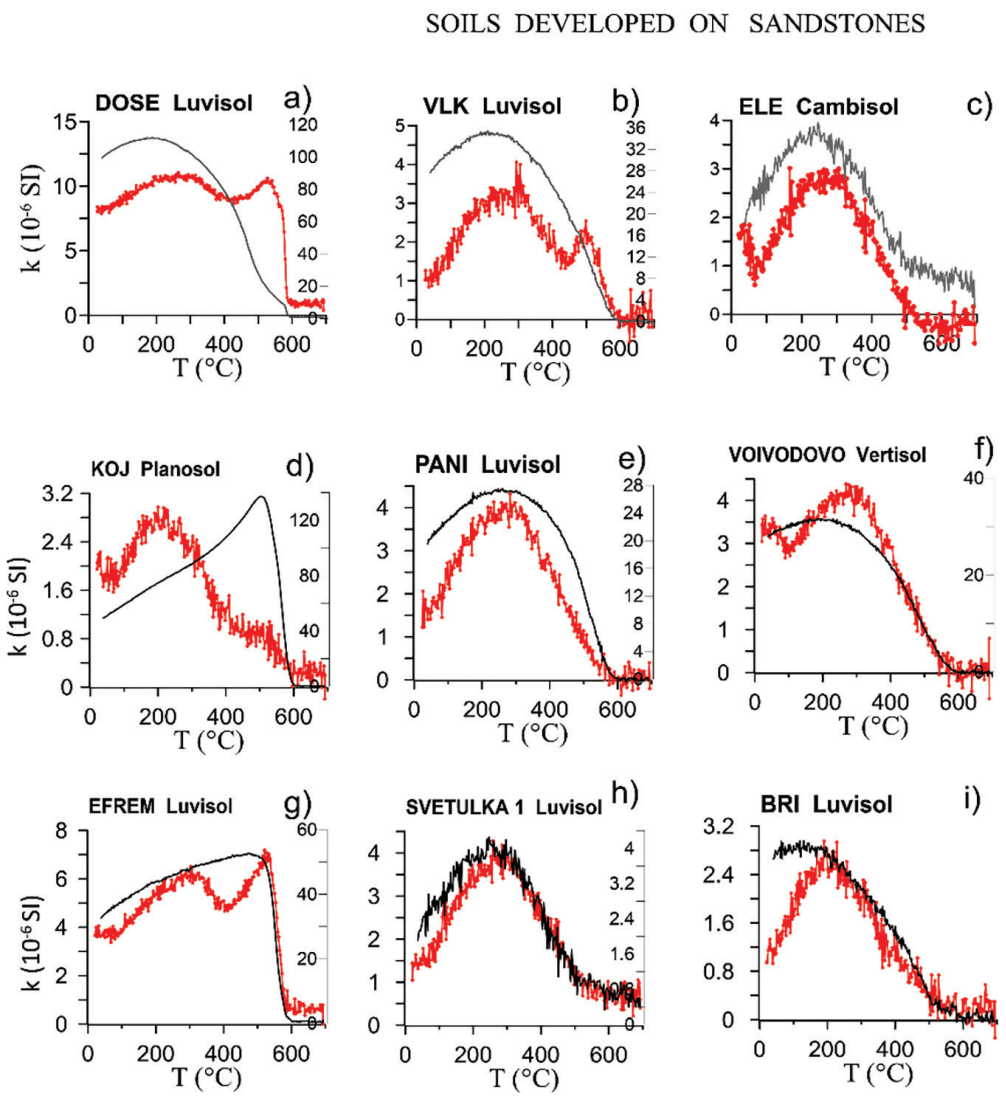

Figure 6. High temperature behavior of magnetic susceptibility for representative samples of soils, developed on sandstones. Heating run is shown in red, cooling run – in black. Right-hand Y-axis (when present) relates to k-values on the cooling curve.

Soils, developed on sandstones (Fig. 6) are the next group of samples. As seen from Fig. 6, for all samples, except DOSE (Fig. 6a) and EFREM (Fig. 6f), the magnetic susceptibility behavior during heating is dominated by the magnetic phase, described previously for the other soils (Figs 3–5) and characterized by a wide hump with maximum at ~ 250–300 °C (Fig. 6). It is considered that this phase is related to the presence of pedogenic fraction fine-grained maghemite (Zhang and Appel 2023) or structural effects in the behavior of ultra-fine grained pigmentary hematite (Chernyshova et al. 2007; Jiang et al. 2014). Elucidation of this non-uniqueness is further tested by coercivity decomposition of Isothermal Remanent Magnetization curves and will be discussed later. In addition to this dominant magnetic phase, magnetite (Fe_3O_4) with Tc of 580 °C is detected for soils VLK (Fig. 6b), KOJ (Fig. 6d) and EFREM (Fig. 6g). Most probably, it originates from the parent rock mineral composition. Low T_N~100 °C is detected in samples ELE, KOJ (Fig. 6c, d) and VOIVODOVO (Fig. 6f), assigned to goethite's presence.

Soils, developed on various kinds of metamorphic rocks (Fig. 7) show thermomagnetic curves, largely similar to those described above.

Distinctly different from all other thermomagnetic curves is the behavior of sample SVETULKA 2 (Fig. 7a). Very strong alteration peak in K is observed on heating above 400 °C, which is related to secondary magnetite's formation. Such transformation behavior is typical for goethite, mixed with organic carbon (Hanesch et al. 2006). Other samples show presence of typical magnetic phases, assigned above to pedogenic maghemite/hematite and (lithogenic) magnetite (Fig. 7b–e).

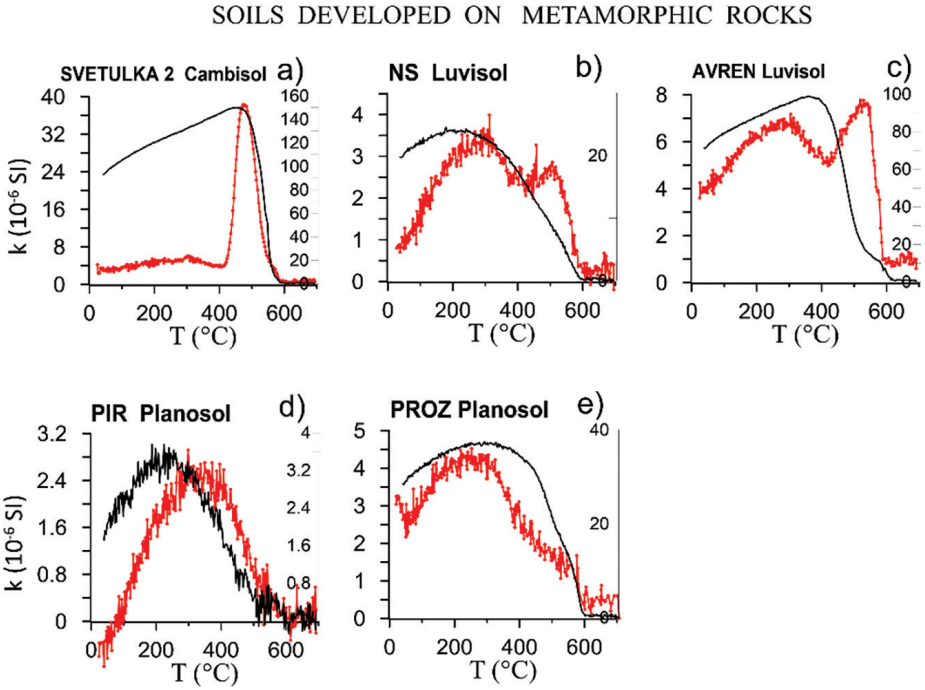

Figure 7. High temperature behavior of magnetic susceptibility for representative samples of soils, developed on metamorphic rocks. Heating run is shown in red, cooling run – in black. Right-hand Y-axis relates to k-values on the cooling curve.

Soils, developed on loosely consolidated parent materials like alluvium and loess (Fig. 8) show more variable thermomagnetic behavior, compared to soils developed on solid rock parent material (Figs 3–7). Soil TRU developed on alluvial materials (Fig. 8a) displays two consecutive strong magnetic transformations – the first one taking place at ~ 200 °C and a second one, starting after 400 °C. This behavior is very similar to the one, described in Hanesch et al. (2006) for soil sample from A-horizon of a Cambisol from southern Germany. Considering the transformation behavior observed, it can be assigned to thermal alterations in ferryhidrite and goethite, respectively (Hanesch et al. 2006). Abundance of unstable Fe-hydroxides in alluvial soils is also confirmed in studies of depth soil profiles (Jordanova 2016). Very low negative K at room temperature for TRU sample is consistent with measurements of bulk standard samples (Suppl. material 2) and is due to dominant presence of quartz sand grains from the parent material, coupled with weak pedogenesis in this soil type (Jordanova 2016). Sharp transformation peak at ~300 °C on the heating curve of soil DRGI (Fig. 8b) can be related to ferryhidrite transformation in the presence of organics (Hanesch et al. 2006). Well expressed magnetite phase is observed on the thermomagnetic curves for the other samples – SPA (devel-

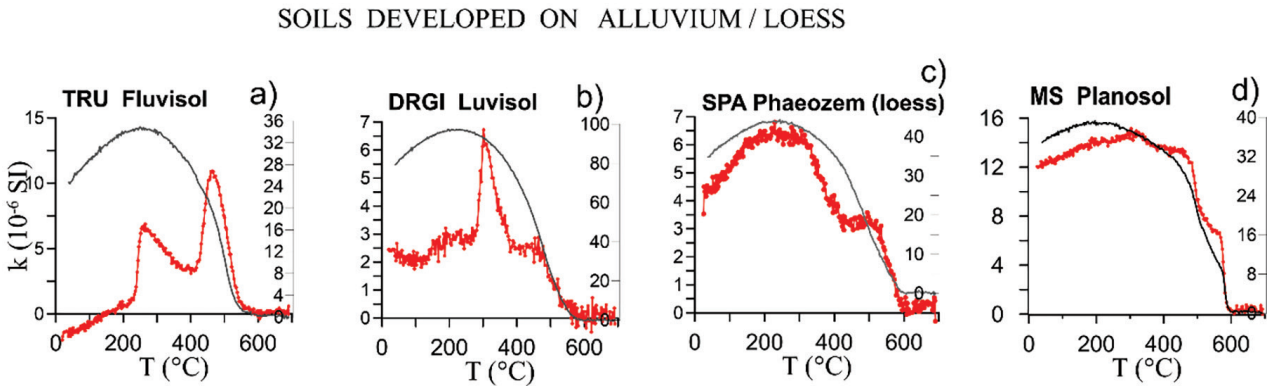

Figure 8. High temperature behavior of magnetic susceptibility for representative samples of soils, developed on alluvial deposits and loess. Heating run is shown in red, cooling run – in black. Right-hand Y-axis relates to k-values on the cooling curve.

oped on loess) and MS (developed on alluvium) (Fig. 8c, d). In addition, hump at ~ 300 °C is also observed on their heating curves, related to maghemite's behavior. All soils, developed on alluvium/loess suffer very strong thermal transformations on heating to 700 °C (Fig. 8), leading to production of secondary magnetite phase.

As revealed in the above discussion, identification of the magnetic phase, expressed as a wide "hump" with a maximum at ~ 250–300 °C is not unique when it is based solely on the high-temperature thermomagnetic analyses. It is possible to link this phase either to SP/SD maghemite or hematite. In addition, thermomagnetic analysis cannot detect hematite, when it is present in a mixture with ferrimagnetic minerals (magnetite, maghemite), except in cases of its prevailing share in the iron oxide pool (Frank and Nowaczyk 2008). In order to solve this ambiguity, a set of 10 samples was selected for analysis of their coercivity spectra through un-mixing the IRM-acquisition curves (Robertson and France 1994; Kruiver et al. 2001). Most of the samples were selected from red-colored soils in order to identify and characterize stable remanence-carrying hematite phase. Results from the coercivity unmixing are shown in Fig. 9. For most samples the IRM-acquisition curve was fitted by two coercivity components and only in samples CRV and SVETULKA1 it was necessary to consider three coercivity components for achieving reasonable data fit (Fig. 9i, j).

Coercivity components were denoted as follows: lowest coercivity C1 (Bh between 27–36 mT); moderate-coercivity C2 (Bh between 52–82 mT); high coercivity C3 (Bh between 580–1100 mT) and very high coercivity C4 (Bh above 2000 mT). They are indicated on Fig. 9 for each specimen. The lowest coercivity component C1 (Fig. 9) is identified in samples ZLI, EFREM, GI, PON and SVETULKA1. This component has a dominant contribution to IRM for samples EFREM, PON and GI, while in the others its share is up to ~20% of the total IRM (Fig. 9). Coercivity of this order is reported for fine grained magnetite/maghemite (Egli 2004). In the other samples the low-coercivity component C2 has coercivities – between 52–82 mT (Fig. 9a–c, f) and cannot be linked to magnetite/maghemite. Thus, we attribute it to a fraction of fine-grained hematite with Al-substitutions in the crystal lattice (Jiang et al. 2014), which is also characterized by low unblocking temperatures. IRM

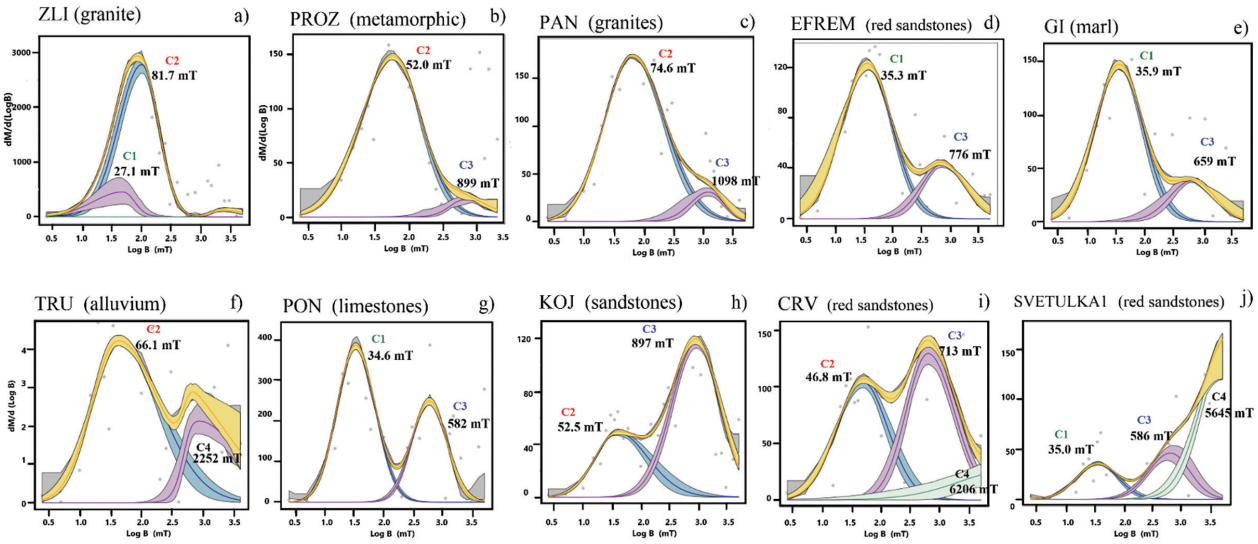

Figure 9. Unmixed coercivity components of IRM-acquisition curves, using MAX UnMix software by Maxbauer et al. (2016). Data points are denoted by dots; cumulative fit together with its confidence band is shaded in yellow. Fitted components with their confidence band are shown in blue, pink and green colors. Bh value (in mT) and component assignment (C1 – C4) for the corresponding component is denoted on each graph.

component C3 with Bh of several hundreds of mT (500–600 mT) (Fig. 9b, d, e, g, h) is typical for hematite (Roberts et al. 2020), while very high Bh (component C4) in samples TRU (Fig. 9f), CRV (Fig. 9i) and SVETULKA1 (Fig. 9j) can be attributed to goethite's presence. Therefore, unmixing analysis of IRM acquisition curves for red-colored topsoils confirmed the presence of two fractions of hematite – first one with relatively low coercivity, characteristic for fine-grained (pedogenic) hematite with Al-substitutions, and a second one, consistent with typical (lithogenic) hematite. Maghemite of low coercivity is also present in part of the samples, together with lithogenic hematite.

Thermomagnetic analysis of magnetic susceptibility of topsoils, utilizing small sample mass, allowed revealing the major mineral magnetic phases, responsible for the soil's magnetic characteristics. In the absence of micro-reducing environment during heating, created by bigger sample amount (Jordanova and Jordanova 2016), thermomagnetic curves for topsoils from Bulgaria demonstrated wide presence of a magnetic phase with low Tc (Tub) (~ 250–300 °C), tentatively attributed to pedogenic maghemite and/or fine-grained hematite with abundant Al-substitutions. This phase is observed in soils, developed on various parent rocks (Figs 3–8), which further supports its pedogenic origin. Another independent confirmation of this conclusion comes from the obtained negative semi-linear regression (Fig. 10) between the calculated relative share of the "hump" phase height to the total magnetic susceptibility from the thermomagnetic curves (Figs 3–8) and the saturation magnetization (Ms), reported in a previous study (Jordanova et al. 2016). No systematic grouping according to the parent rock lithology is observed, thus supporting pedogenic origin of this phase.

Notwithstanding, it is worth mentioning that often in thermomagnetic K-T analyses of intrusive and volcanic rocks, a specific "hump" occurring in the range 200–300 °C is registered (e.g. Georgiev et al. 2014; Guo 2023). It is considered that this low-amplitude change in magnetic susceptibility could

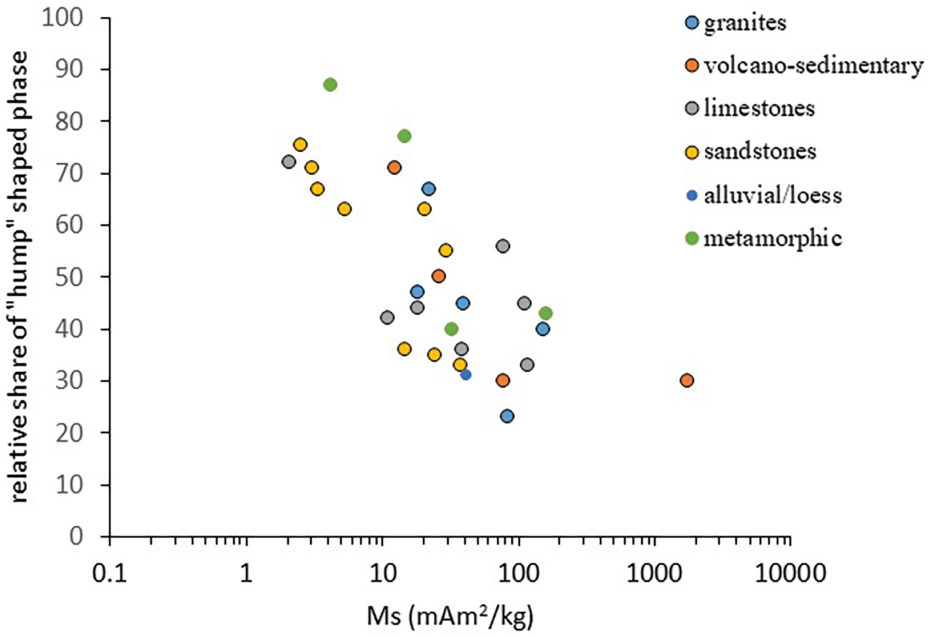

Figure 10. Relation between saturation magnetization (Ms) and the calculated relative share of the "hump"-shaped phase with maximum at 250–300 °C from the thermomagnetic curves. Soils, developed on different parent material, are denoted in different color, according to the legend.

reflect the transformation of trace amount of pyrite which converts to magnetite in this temperature range. Since pyrite is frequently identified by mineralogical methods in such rock types, this interpretation might be feasible. In case of soils reported in the present study, however, the amplitude of the thermomagnetic changes in K in the temperature range up to ~300–400 °C is much higher (Figs 3–5) and we thus favor the interpretation that pedogenic iron oxide fraction is responsible for it. Other Sulfur-containing minerals (pyrrhotite, greigite) show very strong and sharp transformation (Muxworthy et al. 2023), which is not observed for the soils in our study.

Lithogenic magnetic mineral identified through thermomagnetic analyses is most often coarse-grained magnetite. Nevertheless, hematite is detected in a number of red-colored soils, as those, developed on red sandstones (Fig. 6). Iron hydroxhides goethite, ferrihydrite, lepidocrocite are detected more rarely, mainly through their thermal transformation temperature, above which strongly magnetic iron oxide phase is created.

Conclusions

Thermomagnetic analysis of high-temperature behavior of magnetic susceptibility for a collection of topsoils from Bulgaria, developed on various lithologies, showed that it is a powerful tool for identification of iron (oxy)hydroxides' s origin. Using small sample mass, pedogenic fraction of maghemite and/or fine-grained hematite is revealed. This pedogenic fraction is identified in soils, developed on various parent rocks, showing that its origin is related to climatic- and biologically-induced processes in soils. Lithogenic magnetic minerals identified are mostly coarse grained magnetite and hematite.

Acknowledgements

The authors are grateful to the two reviewers for their constructive comments.

Additional information

Conflict of interest

The authors have declared that no competing interests exist.

Ethical statement

No ethical statement was reported.

Funding

This work is supported by the project КП-06-Н34/2 of Bulgarian National Science Fund.

Author contributions

N.J. - data acquisition, analysis and interpretation, manuscript writing; D.J. - data acquisition and analysis, manuscript editing.

Author ORCIDs

Neli Jordanova https://orcid.org/0000-0002-9959-4456
Diana Jordanova https://orcid.org/0000-0003-0595-3153

Data availability

All of the data that support the findings of this study are available in the main text or Supplementary Information.

References

Certini G, Scalenghe R (2011) Anthropogenic soils are the golden spikes for the Anthropocene. Holocene 21(8): 1269–1274. https://doi.org/10.1177/0959683611408454

Chernyshova IV, Hochella MF, Madden AS (2007) Size-dependent structural transformations of hematite nanoparticles. 1. Phase transition. Physical Chemistry and Chemical Physics 9: 1736–1750. https://doi.org/10.1039/b618790k

Cornell R, Schwertmann U (2003) The Iron Oxides. Structure, properties, reactions, occurrence and uses. Weinheim, New York. https://doi.org/10.1002/3527602097

Dearing JA, Hay KL, Baban SMJ, Huddleston A, Wellington E, Loveland P (1996) Magnetic susceptibility of soil: An evaluation of conflicting theories using a national data set. Geophysical Journal International 27(3): 728–734. https://doi.org/10.1111/j.1365-246X.1996.tb04051.x

Declercq Y, Samson R, Van De Vijver E, de Grave J, Tack FMG, De Smedt P (2020) A multiproxy magnetic approach for monitoring large-scale airborne pollution impact. Science of the Total Environment 743: 140718. https://doi.org/10.1016/j.scitotenv.2020.140718

Duminuco P, Messiga B, Riccardi MP (1998) Firing process of natural clays. Some microtextures and related phase compositions. Thermochimica Acta 321: 185–190. https://doi.org/10.1016/S0040-6031(98)00458-4

Dunlop D, Özdemir O (1997) Rock Magnetism. Fundamentals and frontiers. D. Edwards (Ed.), Cambridge Studies in Magnetism, Cambridge University Press. https://doi.org/10.1017/CBO9780511612794

Egli R (2004) Characterization of individual rock magnetic components by analysis of remanence curves. 3. Bacterial magnetite and natural processes in lakes. Physics and Chemistry of the Earth 29: 869–884. https://doi.org/10.1016/j.pce.2004.03.010

Evans M, Heller F (2003) Environmental Magnetism: Principles and Applications of Enviromagnetics. Academic Press, San Diego, CA.

Fialová H, Maier G, Petrovský E, Kapicka A, Boyko T, Scholger R (2006) Magnetic properties of soils from sites with different geological and environmental settings. Journal of Applied Geophysics 59(4): 273–283. https://doi.org/10.1016/j.jappgeo.2005.10.006

Frank U, Nowaczyk NR (2008) Mineral magnetic properties of artificial samples systematically mixed from haematite and magnetite. Geophysical Journal International 175(2): 449–461. https://doi.org/10.1111/j.1365-246X.2008.03821.x

Georgiev N, Henry B, Jordanova N, Froitzheim N, Jordanova D, Ivanov Z, Dimov D (2009) The emplacement mode of upper Cretaceous plutons from the southwestern part of the Sredna Gora Zone (Bulgaria): Structural and AMS study. Geologica Carpathica 60(1): 15–33. https://doi.org/10.2478/v10096-009-0001-8

Georgiev N, Henry B, Jordanova N, Jordanova D, Naydenov K (2014) Emplacement and fabric-forming conditions of plutons from structural and magnetic fabric analysis: A case study of the Plana pluton (Central Bulgaria). Tectonophysics 629: 138–154. https://doi.org/10.1016/j.tecto.2014.02.018

Guo W (2023) Thermal magnetic analysis on iron ores and banded iron formations (BIFs) in the Hamersley Province: Implications of origins of magnetic minerals and iron ores. AIMS Geosciences 9(2): 311–329. https://doi.org/10.3934/geosci.2023017

Hanesch M, Stanjek H, Petersen N (2006) Thermomagnetic measurements of soil iron minerals: the role of organic carbon. Geophysical Journal International 165: 53–61. https://doi.org/10.1111/j.1365-246X.2006.02933.x

Hanesch M, Rantitsch G, Hemetsberger S, Scholger R (2007) Lithological and pedological influences on the magnetic susceptibility of soil: Their consideration in magnetic pollution mapping. Science of the Total Environment 382: 351–363. https://doi.org/10.1016/j.scitotenv.2007.04.007

Henry B, Naydenov K, Dimov D, Jordanova D, Jordanova N (2012) Relations between the emplacement and fabric-forming conditions of the Kapitan-Dimitrievo pluton and the Maritsa shear zone (Central Bulgaria): Magnetic and visible fabrics analysis. International Journal of Earth Sciences 101(3): 747–759. https://doi.org/10.1007/s00531-010-0634-y

Hoffmann V, Knab M, Appel E (1999) Magnetic susceptibility mapping of roadside pollution. Journal of Geochemical Exploration 66(1–2): 313–326. https://doi.org/10.1016/S0375-6742(99)00014-X

Jenny H (1941) Factors of soil formation. A system of quantitative pedology. R. Amundson, Dover Publ. Inc., New York [edition 1994].

Jiang Z, Liu Q, Dekkers MJ, Colombo C, Yu Y, Barrõn V, Torrent J (2014) Ferro and antiferromagnetism of ultrafine-grained hematite. Geochemistry, Geophysics, Geosystems 15(6): 2699–2712. https://doi.org/10.1002/2014GC005377

Jordanova N (2016) Soil Magnetism: Applications in Pedology, Environmental Science and Agriculture, Academic Press (Elsevier), 445 pp. [ISBN:9780128092392]

Jordanova D, Jordanova N (2016) Thermomagnetic behavior of magnetic susceptibility – heating rate and sample size effects. Frontiers in Earth Science 3: [article] 90. https://doi.org/10.3389/feart.2015.00090

Jordanova N, Jordanova D, Petrov P (2016) Soil magnetic properties in Bulgaria at a national scale—Challenges and benefits. Global and Planetary Change 137: 107–122. https://doi.org/10.1016/j.gloplacha.2015.12.015

Kruiver P, Dekkers M, Heslop D (2001) Quantification of magnetic coercivity components by the analysis of acquisition curves of isothermal remanent magnetization. Earth and Planetary Science Letters 189: 269–276. https://doi.org/10.1016/S0012-821X(01)00367-3

Maher B (1998) Magnetic properties of modern soils and Quaternary loessic paleosols: paleoclimatic implications.Palaeogeography, Palaeoclimatology, Palaeoecology 137: 25–54. https://doi.org/10.1016/S0031-0182(97)00103-X

Magiera T, Jabłońska M, Strzyszcz Z, Rachwal M (2011) Morphological and mineralogical forms of technogenic magnetic particles in industrial dusts. Atmospheric Environment 45(25): 4281–4290. https://doi.org/10.1016/j.atmosenv.2011.04.076

Maxbauer DP, Feinberg JM, Fox DL (2016) MAX UnMix: a web application for unmixing magnetic coercivity distributions. Computers and Geoscience 95: 140–145. https://doi.org/10.1016/j.cageo.2016.07.009

Mullins C (1977) Magnetic susceptibility of the soil and its significance in soil science - a review. Journal of Soil Science 28: 223–246. https://doi.org/10.1111/j.1365-2389.1977.tb02232.x

Muxworthy AR, Turney JN, Qi L, Baker EB, Perkins JR and Abdulkarim MA (2023), Interpreting high-temperature magnetic susceptibility data of natural systems. Frontiers in Earth Science 11: 1171200. https://doi.org/10.3389/feart.2023.1171200

O'Reilly W (1984) Rock and Mineral Magnetism. Blakie. Chapman and Hall, Glasgow. https://doi.org/10.1007/978-1-4684-8468-7

Roberts AP, Zhao X, Heslop D, Abrajevitch A, Chen Y-H, Hu P, Jiang Z , Liu Q-S, Pillans BJ (2020) Hematite (α-Fe2O3) quantification in sedimentary magnetism: limitations of existing proxies and ways forward. Geoscience Letters 7: 8. https://doi.org/10.1186/s40562-020-00157-5

Robertson DJ, France DE (1994) Discrimination of remanence-carrying minerals in mixtures, using isothermal remanent magnetisation acquisition curves. Physics of the Earth and Planetary Interior 84: 223–234. https://doi.org/10.1016/0031-9201(94)90074-4

Sardoo ES, Farpoor MH, Mahmoodabadi M, Jafari A (2023) Magnetic susceptibility in soil pedons developed on different parent rocks in Kerman province (Iran). Studia Geophysica et Geodaetica 67: 83–106. https://doi.org/10.1007/s11200-021-0771-8

Théveniaut H, Clarke B (2013) Large scale magnetic susceptibility soil mapping: a proxy for geological mapping and exploration from Bogoso (Ghana), Exploration Geophysics 44(1): 48–55. https://doi.org/10.1071/EG12019

Thompson R, Oldfield F (1986) Environmental Magnetism. Allen & Unwin, London. https://doi.org/10.1007/978-94-011-8036-8

Zhang Q, Appel E (2023) Reversible Thermal Hysteresis in Heating-Cooling Cycles of Magnetic Susceptibility: A Fine Particle Effect of Magnetite, Geophysical Research Letters 50(6): e2023GL102932. https://doi.org/10.1029/2023GL102932

Supplementary material 1

Soil classification (figure)

Authors: Neli Jordanova, Diana Jordanova

Data type: pdf

Copyright notice: This dataset is made available under the Open Database License (http://opendatacommons.org/licenses/odbl/1.0/). The Open Database License (ODbL) is a license agreement intended to allow users to freely share, modify, and use this Dataset while maintaining this same freedom for others, provided that the original source and author(s) are credited.

Link: https://doi.org/10.3897/geostudies.1.e115530.suppl1

Supplementary material 2

Additional data (table)

Authors: Neli Jordanova, Diana Jordanova

Data type: xlsx

Copyright notice: This dataset is made available under the Open Database License (http://opendatacommons.org/licenses/odbl/1.0/). The Open Database License (ODbL) is a license agreement intended to allow users to freely share, modify, and use this Dataset while maintaining this same freedom for others, provided that the original source and author(s) are credited.

Link: https://doi.org/10.3897/geostudies.1.e115530.suppl2